

General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

NASA TECHNICAL MEMORANDUM

NASA TM-77046



STRUCTURE AND GROWTH PROCESS OF VAPOR-GROWN CARBON
FIBERS

Tsuneo Koyama and Morinobu Endo

Translation of "Kiso Seicho Tanso Sen'i Koso to Secho
Katei." Oyo Butsuri, Vol 42, No. 7, 1973, pp. 690-696.

(NASA-TM-77046) STRUCTURE AND GROWTH
PROCESS OF VAPOR-GROWN CARBON FIBERS
(National Aeronautics and Space
Administration) 22 p HC A02/MF A01 CSC 11D

N83-29313

Unclassified
G3/24 12969

STANDARD TITLE PAGE

1. Report No. NASA TM 77046	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle STRUCTURE AND GROWTH PROCESS OF VAPOR-GROWN CARBON FIBERS		5. Report Date APRIL 1983	6. Performing Organization Code
7. Author(s) Tsuneo Koyama and Morinobu Endo		8. Performing Organization Report No.	9. Work Unit No.
10. Performing Organization Name and Address SCITRAN Box 5456 Santa Barbara, CA 93108		11. Contract or Grant No. NASW 3542	12. Type of Report and Period Covered Translation
13. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		14. Sponsoring Agency Code	
15. Supplementary Notes Translation of "Kiso Seicho Tanso Sen'i Koso to Seicho Katei." Oyo Butsuri, Vol. 42, No.7, 1973, pp. 690-696.			
16. Abstract Investigates the structure, effect of heat, and growth process of vapor-grown carbon fibers. The growth process of the carbon fibers could be divided into three stages; nucleation, elongation, and thickening processes. Also, a multi-layered structure can be produced as well as graphitiza- tion.			
ORIGINAL PAGE IS OF POOR QUALITY			
17. Key Words (Selected by Author(s))		18. Distribution Statement	
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified	21. No. of Pages 22
		22. Price	

STRUCTURE AND GROWTH PROCESS OF VAPOR-GROWN CARBON FIBERS

Tsuneo Koyama and Morinobu Endo ⁺

/690*

Carbon fibers having 25 cm in length have been grown successfully, at a relatively low temperature range of about 1000°C, by means of thermal decomposition of vaporized hydrocarbon such as benzene. The structure, effect of heat treatment and growth process were investigated.

These fibers had a turbostratic stacking arrangement of the carbon-hexagon networks, whose apparent crystallite sizes L_a and L_c were about 30-40 Å, and had a high degree of preferred orientation where the c-axes of the graphite-like layers were nearly perpendicular in the fiber axis with an orientation parameter $\Psi^{1/2} = 15^\circ$. From electron microscopic observations, they were found to consist of concentric layers similar to the annual rings of a tree. By heat treatment at high temperatures, the crystallinity and orientation parameter of the fibers were markedly improved. The growth process of the carbon fibers could be divided into three stages; nucleation, elongation and thickening processes.

1. Introduction

Carbon fibers (CF) are widely used as new materials having high strength and high elasticity. Practical application of their composite materials is advancing in the fields of spacecraft and high temperature structural materials.

CF is generally manufactured by carbonization treatment of organic fibers, such as polyacrylonitrile (PAN). On the other hand, fibrous carbon different from these organic CF is obtained by vapor-phase growth. Whisker-like carbon fibers with a thickness of several 100 µm and length of several 10 mm have been observed on a substrate by thermal decomposition

*Translator's note: Numbers in margins refer to foreign text page number.

+ Department of Electrical Engineering, Faculty of Engineering, Shinshu University, Wakasato 500, Nagano City, Japan

of carbon monoxide and various hydrocarbons [1-3] . R. Bacon reports that graphite whiskers were produced with a direct arc in a 92 atmosphere, 3900 K Ar environment [4] .

The authors are carrying out investigative research pertaining to methods for formation of vapor-phase grown CF obtained with the thermal decomposition of hydrocarbons and their many properties and crystallographic characteristics. With their method [5,6] a mixture of hydrocarbon vapors (Atsushi, et al. used benzene here) and H₂ were supplied to the porcelain pipe in the electric furnace and many long fibers were produced on top of a substrate at about 1,000 °C. Wool-like fibers with a length of 25 cm were observed [7] . The thickness of the fibers is usually about 10 µm. However, it is possible to restrict thickness to a range of 1-several 100 µm by adjusting the many treatment conditions. The aspect ratio (length/thickness) should be 10⁴ for optimum application in fiber-reinforced composites.

Vapor-grown CF are fibrous at the time of formation and are different in structure and properties from organic CF obtained by carbonization treatment of fibers extruded from small holes. The CF obtained from this method displays high strength, high elasticity and high electrical conductivity in comparison to those obtained at relatively low temperatures [8,9] and have good heat resistance.

Heretofore, the structure of vapor grown CF, heat treatment effects, and growth process have not always been clear because they developed in small amounts by chance. Moreover, several suggestions have been made with regard to the growth mechanism [10,11,14] . With this method, long fibers are grown with good reproducibility and fibers can be directly observed during formation. Therefore, investigation of the growth process is possible.

2. Experimental Method

The fibers were formed using benzene with the method shown in 6 of the bibliography. The carrier gas H_2 was highly purified through a PD alloy film. The thermostatic section of the electrical furnace was 7 cm and the main section of the graphite pipe (thickness of 37 mm and length of 15 cm) was situated in this section. The temperature was raised to a maximum of $1100^\circ C$.

The heat treatment was carried out by cutting fibers into lengths of 1 cm, placing them in the graphite pipe and heating them with an electron beam in a 2×10^{-5} Torr vacuum. Treatment temperature was within a range of $1300\text{--}2400^\circ C$, retention time was 30 minutes, and temperature elevation rate was about $100^\circ C/min$ at $1000^\circ C$ or less.

Crystallinity was studied using a CuK α ray made monochromatic with an Ni filter. The S-ray powder method, whereby Si powder is mixed as the internal marker specimen, was employed. Computations of the X-ray parameter were made with the method of the Japanese Council for the Promotion of Science [12]. Furthermore, crystallinity was also studied with small angle X-ray diffusion and electron ray diffraction. The degree of orientation of the fibers $\psi_{1/2}$ ($^\circ$) was determined from the intensity curve of the (002) diffracted ray, which was measured as a function of the angle formed between the normal line of the surface and the fiber axis drawn with an irradiated-diffracted X-ray, using fiber specimens.

The surface, end, and cross sectional formation and fine structure of the fibers were studied using electron microscopes and scanning electron microscopes (SEM). The thickness and length

of the fibers were measured by being magnified 150-1500 X under a metallic microscope.

ORIGINAL PAGE IS
OF POOR QUALITY

3. Experimental Results and Considerations

3.1 Structure of Vapor Grown Carbon Fibers

3.1.1 X-Ray Diffraction

The (002) X-ray diffraction image of a vapor grown CF is shown in Figure 1 with curve (a). Curve (b) is the diffraction image of a carbon film that accumulated on the porcelain substrate simultaneous to fiber growth. Curve (c) is explained in 3.2. Other than the (00^l) diffracted ray having a broad peak, neither the fibers nor the carbon films display an obvious diffracted ray.

The apparent size of the crystallite in the c axis direction, $L_c(002)$, is 30-40 Å. The growth temperature with this method is a range of about 1,000-1,300°C. $L_c(002)$ is about constant with temperature. The diffracted ray is unclear and therefore, the apparent size in the direction of the a axis, $L_a(110)$, cannot be determined. When fibers are heat treated at high temperatures, the (110) diffracted ray becomes clear and L_a can be determined. According to the results of heat treatment mentioned in 3.2, L_a is estimated at about 30 Å after growth. These crystallites are large in comparison to organic fibers treated at about 1,000 °C and are the same size as graphite fibers manufactured at about 2,000°C [13].

The distance between planes d_{002} is 3.48 Å and is very wide in comparison to the 3.354 Å of graphite single crystals. According to the Franklin model pertaining to plane conditions of graphite, each plane is a structure where interconnections are completely lost. Moreover, this is doubted since the (112) diffracted ray showing 3 dimensionally arranged planes cannot be measured and therefore, it cannot be said that a graphitic structure is formed with this fiber. The d_{002} of organic CF manufactured at about the same temperature as in this method is much wider than that of this fiber [13].

Judging from a comparison with the diffraction image of carbon films shown in Figure 1, it can be said that the extent of crystallization of the fibers and the films is about the same. The X-ray parameter of this fiber is also in close agreement with the value for thermally decomposed carbon films formed on a substrate with thermal decomposition of methane [14].

According to the Laue X-ray micrographs of the fibers, the (002) diffracted ray becomes arc-shaped and a fiber structure where the graphite planes are almost parallel to the fiber axis is formed [7,9]. Figure 2 curve (a) is the intensity distribution above the (002) diffracted ray and shows the correlation between the diffraction intensity ratio and the angle formed from the fiber axis direction and the c axis direction. The degree of orientation $\psi_{1/2} (^\circ)$, which is defined as the angle width where the intensity ratio is 50%, is about 15 °. A higher orientation than that of organic CF manufactured at about the same temperature is displayed and is similar to that of highly elastic fibers graphitization treated under tension at 3,000°C [13]. It is clear that this fiber has a high degree of orientation in

comparison to its growth temperature. The degree of orientation of the (002) plane of PG which is formed by thermal decomposition at 2,000° C or less is about 30° [15]. It seems that the carbon film that accumulates on the substrate with fiber formation has the same degree of orientation as these PG. CF and carbon films display the same extent of crystallite development. However, it seems that there is a difference in the selective orientation ability.

/692

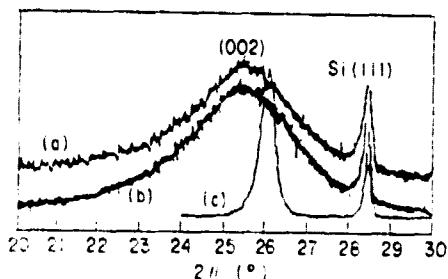


Fig. 1 (002) diffraction profiles. (a) as-grown carbon fibers, (b) carbon film, (c) carbon fibers heat-treated at 2000°C. (111) line of silicon (28.5° in 2θ) is shown as internal standard.

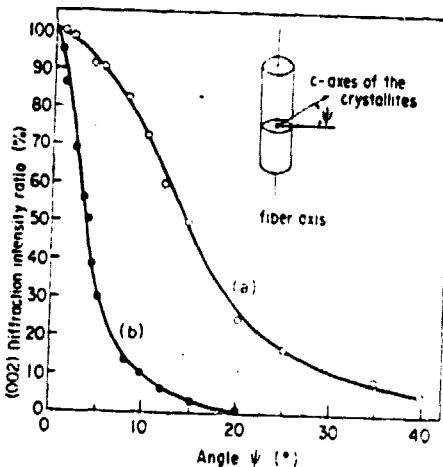


Fig. 2 Representative results of preferred orientation measurements. (a) as-grown carbon fiber, (b) carbon fiber heat-treated at 1900°C.

**ORIGINAL PAGE IS
OF POOR QUALITY**

A small angle X-ray scattering image is shown in Figure 3.

However, almost no small angle scattering is present. On the other hand, intense scattering is seen with PAN and rayon CF [16]. The fibers from this method seem to have a very close structure without any micro holes. This is assumed to be due to the fact that the density of this fiber is 2.03 g/cm^3 , which is large in comparison to that of organic CF.



Fig. 3 X-ray small angle scattering.

3.1.2 Observations with Electron and Scanning Electron Microscopes

The surface of the fibers presents metallic brilliance without any defects, such as cracks, etc. The outside can be divided into a relatively smooth surface and a wavy surface. One example is shown in Figure 4. With a thickness of $10 \mu\text{m}$ or less, the fiber is rugged or wavy and becomes smooth as it becomes thicker. The fact that fine fibers are very rugged in outside appearance is a feature of this fiber.

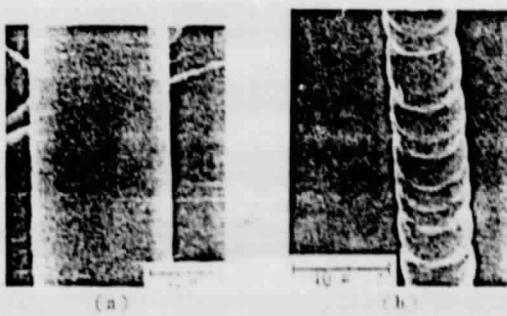


Fig. 4 SEM picture showing the typical surface configuration. (a) smooth surface. (b) rugged surface.

An SEM photograph of the fiber cross-section is shown in Figure 5. A concentrically-layered thin carbon film is formed to produce a shape similar to the annual rings of a tree. The thickness of the film is several 100 Å. On the other hand, there are also cases when a spiral-type cross section is observed. However, a structure of annual tree-like rings where there is no spiraling is seen in highly magnified SEM and stero SEM photographs. Although simultaneous lengthwise and thickness growth are anticipated with a spiral-like structure [4,10], it seems that length and thickness develop in different processes with an annual tree-like ring structure.



Fig. 5 SEM pictures of cross-section of a carbon fiber.

Figure 6(a) is an SEM photograph of the surface of fibers deposited on a graphite substrate. Many round bubbles are present on the carbon film surface and part of the fiber forms a bubble-like structure. Figure 6(b) is the cleaved verticle section of the fiber. The vertical stripes of the fiber are connected to the horizontal stripes of the film and the thick section of the fiber and film deposited on the substrate are formed in the same layer. It seems that this structure is formed by simultaneous deposition of the film on the substrate and fiber surface. The fact that the fiber section is a closed tree-like ring structure and the degree of crystallization of the fiber and film

are the same, which is seen in Figure 1 curves (a) and (b)
can be concluded from this structure.

693



Fig. 6 SEM pictures of (a) surface and (b) cleaved vertical section (1-substrate, 2 deposited carbon film, 3-carbon fiber) of the carbon film deposited on substrate.

A smooth dark and light-striped vertical section and dark spots can be seen along the fiber axis in the transmission electron micrographs of the fiber vertical section shown in Figure 7 (a). A highly magnified bright field image of the fiber core is shown in Figure 7 (b). The vertical strips with a thickness of 100 \AA or less and length of several 1000 \AA are arranged almost parallel to the fiber axis in the dark section. The dark field image, which employed the (002) diffracted ray and is shown in Figure 7(c) corresponds to the vertically striped section. It seems that 1 strip is 1 fibril formed by layering of the long, slender carbon hexagon networks. The thickness of this vertical strip is close to the $L_c(002)$ determined by X-ray diffraction. However, the length is very different from the $L_a(110)$. The linearity of the vertical strip is probably related to the degree of orientation of the crystallite. The fine structure similar to the aforementioned is also seen with rayon, Pan, and pitch CF. It can be said that this fiber is constructed by accumulation of fibrils, as is organic CF[13].

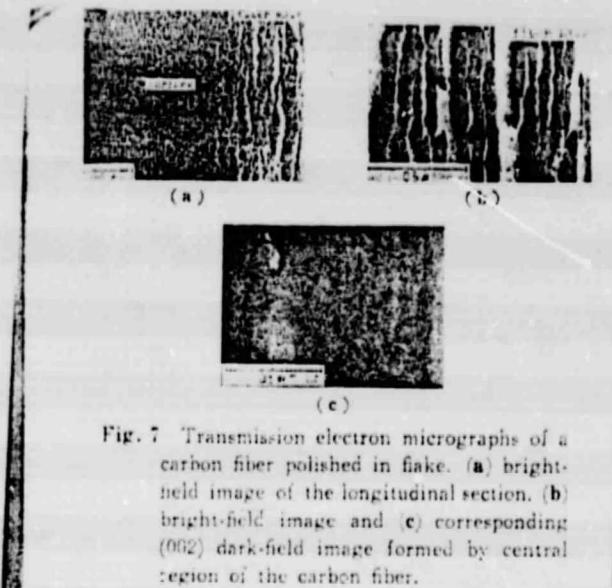


Fig. 7 Transmission electron micrographs of a carbon fiber polished in flake. (a) bright-field image of the longitudinal section, (b) bright-field image and (c) corresponding (002) dark-field image formed by central region of the carbon fiber.

3.2 Heat Treatment of Vapor Grown Carbon Fibers

Crystallization of this fibers seems to be accelerated with heat treatment and therefore, its graphitization ability will be mentioned next.

An X-ray diffraction image of fibers treated at 2,000°C is shown in Figure 1 curve (c). When compared to the untreated fiber of curve (a), crystallinity is greatly enhanced with heat treatment. The correlation between heat treatment temperature and X-ray parameters is shown in Figure 8. Apparent size of the crystallites $L_c(002)$ and $L_a(110)$ increases with an increase in treatment temperature. There is a tendency for the apparent size to be 5 times greater than that of as grown fibers with heat treatment at 2,000°C. Plane spacing d_{002} decreases with temperature and the plane arrangement changes from a disordered layer structure to a graphitic structure. This is obvious because of the fact that the (112) diffracted ray that could not be measured appeared with grown fibers with an increase in treatment temperature. 3 dimensional arrangement of the planes begins at about 1500°C. Factor g of Mering [17], which shows the extent of graphitization, becomes 0.81 with treatment at 2400°C.

Furthermore, it seems that when heat treatment is performed at high temperatures, the aforementioned X-ray parameter is changed with elongation of the curve in Figure 8 and is close to the value of graphite single crystals.

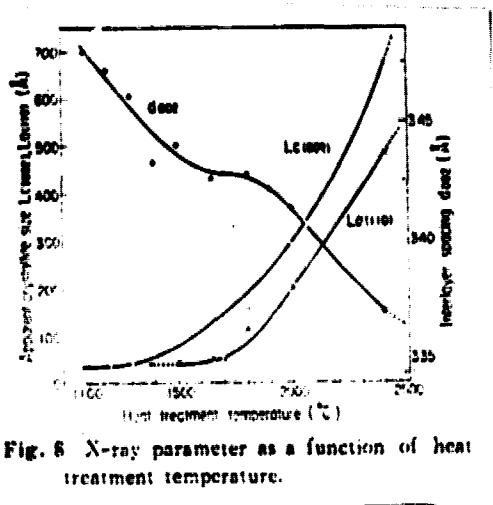


Fig. 8 X-ray parameter as a function of heat treatment temperature.

Figure 9 shows the correlation between the degree of orientation and heat treatment temperature. The degree of orientation is less than 2 with a heat treatment temperature of 2400° C. The orientation curve of fibers heat treated at 1900° C is shown in Figure 2 curve (b). With heat treated fibers there are very few fluctuations in the c axis orientation of the crystallite. The degree of orientation of PAN CF which was graphitized under tension at 3000° C is 6-10°[13] and it is clear that this fiber has a very high orientation only when heat treated at relatively low temperatures. This seems to be due to the fact that the fibers did have a high selective orientation ability during formation.

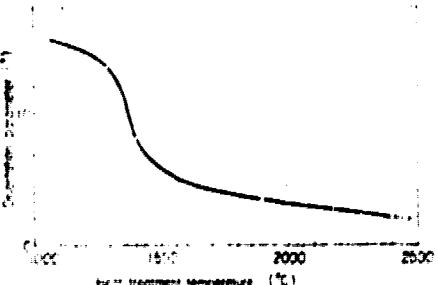


Fig. 9 Orientation parameter vs. heat treatment temperature.

The electron ray diffraction images of grown fibers and fibers treated at 2000 °C are shown in Figure 10. The electron ray diameter is $0.8 \mu\text{m}^2$. With this fiber, a highly crystallized section is present in the grown state and a localized single crystal pattern is observed [7]. However, the multicrystal pattern shown in (a) is usually obtained. Crystallization is greatly enhanced in heat treated fibers.

/694

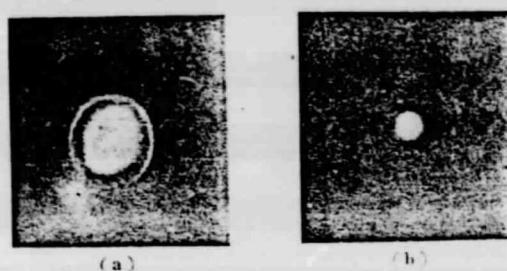


Fig. 10 Electron diffraction patterns. (a) as-grown carbon fiber. (b) heat-treated at 2000°C.

The properties of fibers treated at 2400 °C are shown in Table 1. Electrical resistivity along the fiber axis is 1×10^{-4} cm at room temperature and is similar to the value of single graphite crystals along the a-b plane [18]. Mechanically grown fibers are brittle and break easily, but heat treated fibers are pliable and difficult to break. Moreover, the increase in tensile strength is remarkable. These properties are similar to those of graphite whiskers [4].

Table 1 Characteristics of the carbon fibers.

Carbon fibers	Electrical resistivity (Ωcm)	Tensile strength (kg/cm^2)	Young's modulus (kg/cm^2)
as grown	$1.0 \sim 1.6 \times 10^{-4}$	15 (diameter $15 \mu\text{m}$)	$2,000 \sim 4,000$
heat-treated at 2400°C	$8 \sim 15 \times 10^{-4}$	50	$2,000 \sim 4,000$

From the afo mentioned it is clear that this fiber has graphitization ability and its degree of orientation is improved by heat treatment. Consequently, it seems that fibers similar to

graphite whiskers [4] can be formed with heat treatment at even higher temperatures.

3.3 Growth Processes

With this method the fibers develop when hydrocarbons are supplied before the substrate temperature reaches the established temperature (1100°C or more) and almost no fibers are observed when the initial partial pressure of the hydrocarbons is not increased [6].

A photograph of carbon fibers growing in the furnace with an increase in temperature is shown in Figure 11. The fibers grown uniformly on the inside wall of the substrate, are inclined $50\text{--}60^{\circ}$ from the pipe, and contact the substrate surface. Figure 12 shows the correlation between thermal decomposition time and substrate temperature, fiber thickness and fiber length when the initial partial pressure of the benzene is increased.

Standard formation time was made the point when mixed gas was introduced after the substrate temperature reached 950°C . Thickness and length were measured with regard to fibers that developed in the desired position at the substrate core. An inflection point pertaining to growth at about 1040°C is seen in the figure.

Growth of the fibers is divided into the process of lengthwise elongation at a constant thickness and thickening at a constant length. Moreover, benzene partial pressure must be present at a temperature of 1010°C or less for fibers to grow. In addition, growth of fibers is not observed at less than 1010°C .

Therefore, nucleation is regarded as the initial fiber growth stage. From the aforementioned, it can be said the vapor growth of fibers is divided into the stages of nucleation at less than 1010°C , elongation at $1010\text{--}1040^{\circ}\text{C}$, and thickening at more than 1040°C . These temperature ranges vary with the amount of hydrogen and partial pressure of the benzene. There is a tendency for the

temperature and are lower with an increase in benzene partial pressure.

The carbon film deposits on the substrate during the nucleation period and is very thin at $0.1 \mu\text{m}$ or less. When an Mo plate or etched Si crystal are used as the substrate, the fiber grows from the section with the smallest island-shaped protrusion on the film. It seems that this protrusion is formed from small soot-like particles.



Fig. 11 Carbon fibers growing in the apparatus.

In figure 12 the elongation rate of the elongation process is about 1 mm/min and is about equal to the elongation rate observed from the outside of the furnace window. The thickness is about constant at $1 \mu\text{m}$ or less. Necking of this fiber is remarkable and the thickness is measured at the thickest section. It is possible to restrict the length of the fiber by adjusting the elongation process. When the many conditions for fiber formation are suitable, elongation occurs within the thermostatic section of the furnace and $20\text{-}25 \text{ cm}$ wool-like fibers are observed [7].

/695

The thickening rate during the thickening process gradually decreases at about $0.2 \mu\text{m}/\text{min}$. The thickening rate increases when the benzene partial pressure increases. Although the maximum temperature during the thickening process is unclear, many granule-like protrusions are formed on the fiber surface at 1300°C or more and the smooth surface is lost.

Photographs of fibers during the elongation and thickening processes are shown in Figure 13. During the elongation process the fibers are irregular in shape and necking is seen. The ends of the fibers are pointed. A branched section and net section can be seen. During the thickening process, necking gradually disappears and the fibers becomes smooth. The ends of the fibers are round. This may be due to the fact that during the thickening process the fibers which initially displayed extreme necking become covered. The 2 types of external appearances in Figure 4 may also be due to the differences in the thickening processes.

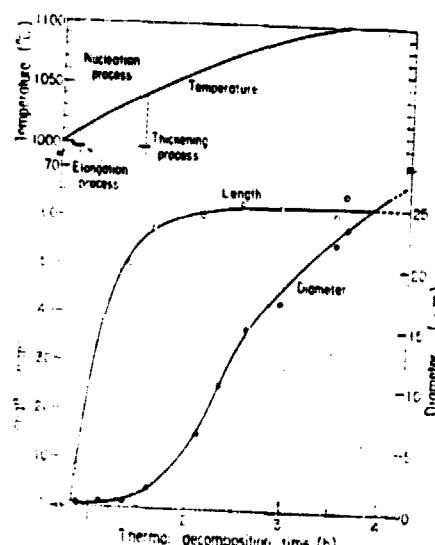


Fig. 12 Plotting the value of measured thickness and length of typical fiber as a function of thermal decomposition time.

ORIGINAL PAGE IS
OF POOR QUALITY



Fig. 13 SEM pictures showing the typical aspect of each growth stage. (a) fibers in elongation process, (b) fibers in incipient stage and (c) in last stage of thickening process.

From the aforementioned it seems that slender fibers are produced after nucleation on the substrate and then the thickening processes takes over with the formation of a 2 dimensional film on the fiber. A tree-like ringed structure and layered structure where the fibers and film are connected can be observed with this process. Moreover, when a carbon film is formed on the substrate, the crystallite c axis becomes perpendicular to the deposition surface [14]. Therefore, with this fiber, thickening occurs with the c axis perpendicular to the fiber axis and c axis orientation is obtained.

4. Tests

As a result of studying the structure of growth processes, it seems that CF fibers from this method have an annual tree ring structure where the carbon thin film having good orientation ability is layered concentrically around the fiber axis. As observed from this structure, CF and the thin film are similar in properties. The resistivity along the fiber axis at room temperature is in close agreement with the value of the carbon film obtained with thermal decompoaisiton of methane, $1-1.8 \times 10^{-3}$ cm [14]. Moreover, the two densities are also similar [14].

The modulus of elasticity of the carbon fibers is regarded as a function of the degree of orientation and the tensile strength of the fibers is regarded as a function of the degree of orientation and size of the crystallite [19]. The fact that

the size of the crystallite and degree of orientation of this fiber is about the same as that of organic CF manufactured at 2000-3000°C was displayed. However, its mechanical properties are also similar to those of PAN CF treated at 2600 °C [19] and correspond to crystallinity.

Growth of the fibers consists of the nucleation, elongation and thickening processes. Thickening occurs with film coating of the fibers. According to X-ray diffraction immages of the carbon fibers, crystallinity is poor in comparison to fibers that have been through the thickening process. It seems that during the fiber formation stage, the fibers are similar to irregular shaped carbon fibers, but crystallization is enhanced during thickening.

Dislocation and impurities were not noticed during growth of the carbon fibers. Fibers were formed by supplying a liquid polycyclic aromatic compound made at a high temperature to the small protrusions on the substrate. Condensation formed along the gas current in the reaction pipe to form fibers and there seems to be a gradual change to irregular carbon fibers, which seems to be the stage prior to graphitization. Moreover, it is assumed that the elongation process is the process where the polycyclid aromatic compound becomes super saturated and reaches equilibrium. In addition, many tests are not being carried out on the aforementioned nucleation process. This will be a topic for future research.

5. Conclusion

The structure of fibers produced by thermal decomposition of benzene, heat treatment results, and growth processes were studied. These results are summarized as follows.

1) This fiber has a disordered layer structure and crystallite apparent size and plane spacings of $L_c(002) = 30-40 \text{ \AA}$, $L_a(110) = 30 \text{ \AA}$, and $d_{002} = 3.48 \text{ \AA}$. Moreover, it has a high degree of selective orientation ability and the c axis of the carbon hexagon network is oriented at almost a right angle with the fiber axis.

The degree of orientation is $\psi_{1/2} = 15^\circ$.

2) The fiber has an annual tree ring structure where the carbon thin film is closely layered around the fiber axis.

3) The fiber which has graphitization ability and crystallinity is greatly enhanced with heat treatment. Moreover, orientation is also improved.

4) Growth of the fibers from this method is divided into the nucleation, elongation, and thickening stages. It is possible to control length and thickness of the fibers by adjusting the thermal decomposition time in each of the respective stages.

From the aforementioned, it seems that a multilayered structure can be produced with the surface coverings. Moreover, graphitization is also possible, and application in composite materials is anticipated.

In conclusion, we would like to thank Professor Otani, Professor Kato, and Professor Koakira for their help in these experiments. We would also like to express our appreciation to Nihon Denshi Co., Ltd. Rigaku Denki Co., Ltd., and Mr. Seimori, Mr. Seimizu, and Mr. Kinto of Osaka University.

- [1] L.J.E. Hogger, E. Stering and J.T. McCartney. J. Phys. Chem. Vol. 59, (1955) p. 1153.
- [2] R. Weisbeck: Carbon, Vol. 9, (1971) p. 525.
- [3] E. Fitzer, W. Fritz and B. Rhee: International Carbon Conference (1972) p. 288.
- [4] R. Bacon. J. Appl. Phys., Vol. 31, (1960) p. 283.
- [5] Koyama, et al.: Japanese Patent No. 487828.
- [6] Koyama, et al.: Oyo Butsuri, Vol. 11, (1963) p. 857.
- [7] T. Koyama, Carbon, Vol. 10 (1972) p. 757.
- [8] T. Koyama, M. Endo, S. Maruyama. Proc. 14th Japan Cong. Material Res., (1971) p. 210.
- [9] T. Koyama, M. Endo, Y. Onuma. Japan J. appl. Phys., Vol. 11 (1972) p. 445.
- [10] G.W. Sears. J. appl. Phys. Vol. 31 (1959) p. 358.
- [11] E. Fitzer, H. Schlesinger. Berichte der Deutschen Keramischen Gesellschaft V, 43 (1966) 209.
- [12] Japanese Council for the Promotion of Science 117th Convention: Tanso, Vol. 36 (1963) p. 25.
- [13] Otani, et al.: "Carbon Fibers" (edited by Kindai Co., 1973, 3rd ed.) 47 pp.
- [14] R. O. Grisdale, A.C. Peister, W. van Roosbroeck: Bell Syst. tech. J., Vol. 30 (1951) p. 271.
- [15] Sekii, et al.: "Science of New Industrial Materials", (Kanaharby Publishers, 1967), p. 180.
- [16] E. Fitzer, A.K. Fiedler, D.J. Muller. Chemie Ingenieur Technik, Vol. 16, (1971) p. 923.
- [17] Suijima, et al.: "Carbon Materials", (Kyoritsu Publishers, 1970), p. 87.
- [18] D. E. Soule: Phys. Rev. Vol. 112 (1958) p. 698.
- [19] Tanishi: Tanso, Vol. 66 (1971) p. 107.